structural descriptors those that best fit the data. The result is that only a few, well-suited descriptors are sufficient to catalogue and/or predict the activity of many molecules.

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Orbital Interactions in Some Polycycloalkyl Halides: A Photoelectron Spectroscopic Study

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Abstract: The He I photoelectron spectra of tricyclo[3.1.1.0^{3,6}]heptane and its 6-bromo and 6-iodo derivatives and of 1-bromo- and 1-iodo- cubane and adamantane have been measured. The low-ionization energy region of each alkyl halide spectrum shows considerable variations from the simple patterns observed for acyclic alkyl halides. The competition between spin–orbit coupling and conjugative effects which characterizes ionizations involving the halogen lone-pair orbitals is examined by reference to He II spectral measurements. Assignment of the spectra is facilitated by ab initio molecular orbital calculations based on a valence-electron model-potential method. In 1-bromotricyclo[3.1.1.0^{3,6}]heptane and bromocubane the lone-pair bromine orbitals, n_{Br}, appear in two ionization bands involving doubly degenerate e orbitals with respectively antisymmetric and symmetric admixtures of alkane orbitals. In 1-bromoadamantane and 1-iodoadamantane the σ_{CX} bonding character is shared between two orbitals of a_1 symmetry. In each of the iodo compounds the first ionization energy is associated predominantly with iodine character, whereas in the bromo compounds, the first photoelectron band is of varying bromine character. In 6-bromotricyclo[3.1.1.0.^{3,6}]heptane the first band is of alkane character.

The study of alkyl halides by He I photoelectron (PE) spectroscopy has been confined mainly to the smaller acyclic systems up to and including the isomers of the butyl halides.[1-7] Among the monocyclic alkyl halides, cyclopropyl and cyclobutyl bromides have been included in a study of the competition between spin–orbit coupling and conjugation effects.[1] A recent study on some bromo and iodo bicycloalkanes examined the same effects.[8] However, among the polycyclic alkyl halides, only 1-bromoadamantane has been investigated.[9]

The He I PE spectra of alkyl halides (excluding alkyl fluorides) are characterized by two main features. First, the low ionization energy (IE) bands, attributed to the photoejection of electrons from molecular orbitals (MOs) localized on the halogen atom, normally feature an intense doublet caused by spin–orbit (SO) coupling effects in the molecular ions. The magnitude of the splitting and the variation in sharpness of these bands provide a measure of the interaction between halogen and alkane orbitals. The admixture of alkane character in these orbitals can be shown by a He I/He II relative intensity analysis when He II PE data are available.

Second, the comparison of the PE spectrum of an alkyl halide with that of its parent alkane normally shows the simple stabilizing effect of halogen substitution in increasing the alkane IEs, with, for example, bromine producing larger IE shifts than iodine owing to its higher electronegativity.

This basic description, which is generally accurate for the acyclic bromo and iodo alkanes, is varied in the case of many cyclic alkyl halides. In cyclopropyl bromide, the lone-pair band at lower IE is considerably broadened through conjugative interaction with cyclopropyl orbitals, and its separation from the sharp second band is somewhat greater than that expected by SO coupling effects alone. In 1-bromoadamantane,[9] the characteristic SO doublet is lost, caused by a strong interaction of halogen and alkane orbitals which are proximate in energy. By comparison the bromobicycloalkanes[8] show the SO split peaks with the magnitude of the splitting decreasing in going from 1-bromobicyclo[2.1.1]hexane to 1-bromobicyclo[2.2.1]heptane to 1-bromobicyclo[2.2.2]octane. Together with increases in the breadth of these bands through the series, this indicates increases in conjugative interaction of alkane orbitals with the nonbonding bromine orbitals.

So in large polycyclic alkanes, particularly where ring strain leads to low IE bands in the PE spectra, such interactions are likely to be common. In certain polycycloalkyl halides nonbonding halogen orbitals may not only lose their localized identity, but may not even be associated with the first ionization band of the molecule.

The bromo and iodo polycycloalkanes included in this study are 6-bromotricyclo[3.1.1.0^{3,6}]heptane (**1b**), 6-iodotricyclo[3.1.1.0^{3,6}]heptane (**1c**), bromocubane (**2b**), iodocubane (**2c**),

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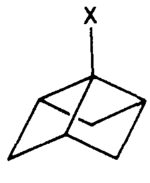
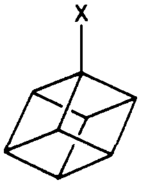
(1) F. Brogli and E. Heilbronner, *Helv. Chim. Acta*, **54**, 1423 (1971).
(2) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle in "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970.
(3) J. L. Ragle, I. A. Stenhouse, D. C. Frost, and C. A. McDowell, *J. Chem. Phys.* **53**, 178 (1970).
(4) J. A. Hashmall and E. Heilbronner, *Angew. Chem. Int. Ed. Engl.*, **9**, 305 (1970).
(5) A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.*, **43**, 375 (1971).
(6) K. Kimura, S. Katsumata, Y. Achiba, H. Matsumoto, and S. Nagakura, *Bull. Chem. Soc. Jpn.* **46**, 373 (1973).
(7) R. G. Dromey and J. B. Peel, *J. Mol. Struct.* **23**, 53 (1974).
(8) E. W. Della, R. S. Abeywickrema, M. K. Livett, and J. B. Peel, *J. Chem. Soc., Perkin Trans.*, in press.
(9) S. D. Worley, G. D. Mateescu, C. W. McFarland, R. C. Fort, and C. F. Sheley, *J. Am. Chem. Soc.*, **95**, 7580 (1973).

0002-7863/84/1506-7321$01.50/0

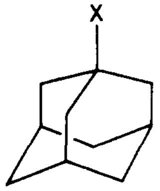
1-bromoadamantane (**3b**), and 1-iodoadamantane (**3c**). Relevant PE studies of the parent alkanes, cubane (pentacyclo-[4.2.0^{2,5}.0^{3,8}.0^{4,7}]octane),[10] and adamantane (tricyclo[3.3.1.1^{3,7}]-decane)[9,11-13] have been reported. The PE spectrum of tricyclo-[3.1.1.0^{3,6}]heptane has not previously been reported so its He I spectrum has been measured for this study.



1a.b,c



2a,b,c



3a,b,c

a. X=H ; b. X=Br ; c. X=I

Experimental Section

The six halides studied were prepared by a variety of techniques, but most commonly by decarboxylative halogenation of the bridgehead carboxylic acids.[14,15] The PE spectra were measured on a double-chamber instrument[16] at temperatures up to 80 °C with appropriate mixtures of methyl iodide, 1,3-butadiene, acetylene, and nitrogen used for calibration of the IE scale. Both He I and He II spectra were obtained, except for **1b** where the small sample available only allowed for a He I measurement. This sample contained bromoform contaminant so spectrum substraction was used to eliminate impurity bands in the measured spectrum. The resulting spectrum of ('pure') **1b** in Figure 1b consequently shows some spurious peaks, notably at 11.2 eV. The 1-h time-averaged 512-point He I spectra are shown in Figures 1, 3, and 5, and single-sweep He II spectra of **2b** and **2c** are included in Figure 4.

Calculations.

In order to assess the effect of halogen substitution on the electronic structure of the parent alkanes, molecular orbital (MO) calculations were performed on each alkane and its bromo and iodo derivatives. All-electron ab initio MO programs do not routinely accommodate molecules containing bromine or iodine, so the valence-electron only model-potential (VEOMP) MO method[17,18] was used. This ab initio method, which is specially designed for calculations on molecules containing heavy atoms, is based on the all-electron GAUSSIAN 70 program[19] and uses a minimum valence STO-3G basis. The method is nonempirical and involves a valence-electron Hamiltonian including a core-pseudopotential and screening function. It is able to produce orbital energies and equilibrium geometries in good agreement with the corresponding all-electron calculations, in particular, for small molecules of first-,[17] second-,[18] and third-row[20] atoms. The minimum basis sets for Br and I were extended to bring the relative energies of alkane and halogen orbitals into better correspondence when the Koopmans approximation is used with experimental IEs. The minimum STO-3G basis performs less adequately for halogen atoms than for hydrocarbons, but additional valence 4s and 4p functions ($\zeta = 0.5$) for Br and 5s and 5p functions ($\zeta = 1.0$) for I are sufficient to provide an acceptable stabilization of the halogen valence orbitals.

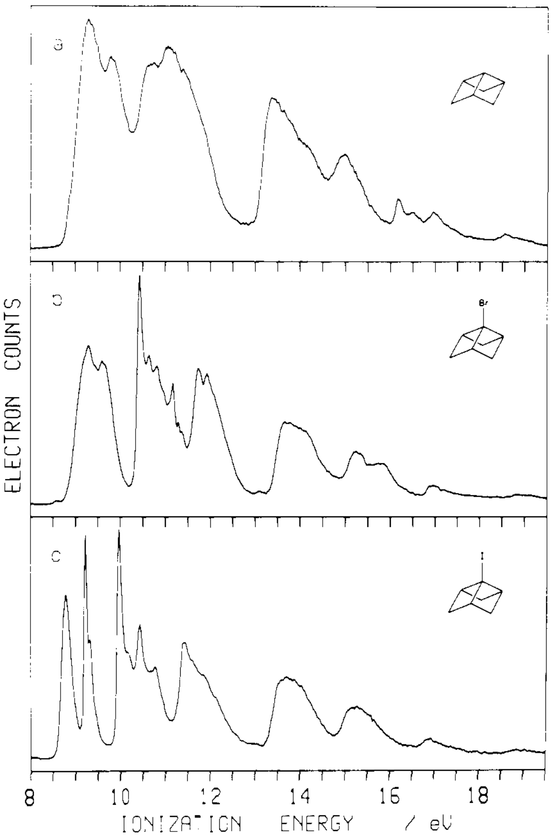


Figure 1. The He I photoelectron spectra of (a) tricyclo[3.1.1.0^{3,6}]heptane, (b) 6-bromotricyclo[3.1.1.0^{3,6}]heptane, and (c) 6-iodotricyclo[3.1.1.0^{3,6}]heptane.

While a MO calculation of each ground-state molecule is able to represent the conjugative interaction between halogen and alkane orbitals, the effects of spin–orbit coupling can be approximated by performing a semiempirical calculation using the relevant atomic splitting parameters with the self-consistent closed-shell wave function. This procedure,[21] where the molecular Hamiltonian is amended with a one-electron spin–orbit interaction operator, simulates the relevant ion states via the Koopmans' approximation. Because it includes both first- and second-order contributions, it is useful in deriving SO shifts for the IEs of molecules of lower than threefold symmetry. While all the polycycloalkyl halides considered here are of C_{3v} symmetry and are expected to show splitting in their halogen bands based mainly on spin–orbit effects, the inclusion of second-order contributions can provide additional conjugative effects.

Of the molecules studied, only cubane (of O_h symmetry) has a reliable experimental geometry.[22] For adamantane, an unstrained geometry of T_d symmetry, based on standard bond lengths and tetrahedral angles is usually used. However, while tricyclo[3.1.1.0^{3,6}]heptane is expected to be of C_{3v} symmetry with a skeleton equivalent to that of cubane with a single carbon bridgehead removed, it is likely to be less strained than cubane. Accordingly, ab initio optimized (STO-3G) geometries[23] were obtained for the three alkanes and used in calculations on the bromo and iodo cycloalkanes with standard C–Br (1.94 Å) and C–I (2.14 Å) bond lengths. The STO-3G optimized bond lengths

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(10) P. Bischof, P. E. Eaton, R. Gleiter, E. Heilbronner, T. B. Jones, H. Musso, A. Schmelzer, and R. Stober, *Helv. Chim. Acta*, **61**, 547 (1978).

(11) R. Boschi, W. Schmidt, R. J. Suffolk, B. T. Wilkins, H. J. Lempka, and J. N. A. Ridyard, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 377 (1973).

(12) G. Bieri, F. Burger, E. Heilbronner, and J. P. Maier, *Helv. Chim. Acta*, **60**, 2213 (1977).

(13) B. Kovac and L. Klasinc, *Croat. Chem. Acta*, **51**, 55 (1978).

(14) For synthesis of the bromides **1b** and **2b**: E. W. Della and H. K. Patney, *Synthesis*, 251 (1976); of **3b**: R. S. Abeywickrema and E. W. Della, *Org. Prep. Proced.* Int., **12**, 357 (1980).

(15) For synthesis of the iodides (**1c** → **3c**): R. S. Abeywickrema and E. W. Della, *J. Org. Chem.*, **45**, 4226 (1980).

(16) E. Nagy-Felsobuki and J. B. Peel, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1927 (1978).

(17) E. Nagy-Felsobuki and J. B. Peel, *Aust. J. Chem.*, **31**, 2571 (1978).

(18) E. Nagy-Felsobuki and J. B. Peel, *J. Chem. Soc. Faraday Trans. 2*, **74**, 2204 (1978).

(19) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, *QCPE*, **10**, 236 (1973).

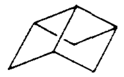
(20) E. Nagy-Felsobuki and J. B. Peel, *Chem. Phys.*, **45**, 189 (1980).

(21) R. G. Hyde and J. B. Peel, *Mol. Phys.*, **33**, 887 (1977).

(22) E. B. Fleischer, *J. Am. Chem. Soc.*, **86**, 3890 (1964).

(23) GAUSSIAN 80: J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, *QCPE*, **15**, 446 (1981).

Table I. Comparison of Experimental and Calculated Vertical Ionization Energies (in eV) and Molecular Orbital Assignment (C_{3v}) of Tricyclo[3.1.1.0^{3,6}]heptane (1a)



exptl IE[a]	assignment MO[b]	STO-3G $-\epsilon$[c]
9.3 9.8	6e	9.25
10.7	6a$_1$	10.50
11.1	5e	11.10
11.5	1a$_2$	11.10
13.4	4e	14.04
13.9	5a$_1$	14.74
14.9	3e	15.50
16.2	4a$_1$	17.40
16.9	3a$_1$	18.04
18.5	2e	20.62

[a] Accuracies vary between ±0.02 and ±0.1 eV. [b] Orbital numbering within the valence shell for C_{3v} symmetry. [c] For the optimized STO-3G geometry.

for cubane (C–C 1.561 Å, C–H 1.086 Å) and adamantane (C–C 1.546 Å, C–H 1.088–1.089 Å) show small differences arising from geometric strain. The optimized bond lengths for tricyclo[3.3.1.0^{3,6}]heptane (C–C 1.559 and 1.552 Å, C–H 1.085–1.088 Å) are indicative of less strain than in cubane, as is the calculated out-of-plane puckering angle of 16.4° for each C_4 ring. This is larger than the puckering angle of 8.0° obtained for cyclobutane itself. More importantly this distorted geometry of tricyclo[3.1.1.0^{3,6}]heptane is lower in total energy by 95 kcal mol^{-1} compared with a geometry derived from that of cubane.

Discussion

The assignment of each He I photoelectron spectrum is illustrated by reference to the calculated molecular orbitals and their eigenvalues.

Tricyclo[3.1.1.0^{3,6}]heptane (1a). Since the molecular structure of **1a** is related to that of **2a**, their PE spectra should show parallel features. This expectation is fulfilled in the He I PE spectrum of **1a** shown in Figure 1a and illustrated by correlation of the experimental IEs and ab initio eigenvalues of **1a** and **2a** in Figure 2.

The spectrum may conveniently by partitioned into three regions. From 9 to 13 eV appear bands which result from ionization of MOs derived from the uppermost t_{2g} and t_{2u} MOs of **2a**. The relative band intensities indicate that the six cationic states are grouped 2:4 in this region; this is consistent with the STO-3G MO data given in Table I. Excitation of Jahn–Teller distorting vibrations is likely to be responsible for lifting the degeneracy of the E cationic state at lowest IE, yielding a double maximum for the first PE band. It is notable that symmetry prohibits any contribution to the $1a_2$ MO from the carbon atom located on the axis of symmetry.

The grouping of 4e, 3e, and $5a_1$ MOs in the IE region from 13 to 16 eV is derived from e_g and t_{1u} MOs of **2a** whose IEs are centered at 14 eV. The **2a** e_g MO is composed entirely of C–C bonding contributions. This attribute is lost in the reduction of symmetry from O_h for **2a** to C_{3v} for **1a**. The distinctive fine structure of the PE band produced by electron ejection from the a_{2u} MO of cubane is retained in the PE spectrum of **1a** where a vibrational spacing of 2400 ± 200 cm^{-1} is observed on the PE band at 16.2 eV. This band can then be unambiguously assigned to ionization of the $4a_1$ MO which excites a C–H stretching vibration. The sensitivity of the calculated eigenvalues to changes in geometry is illustrated by the theoretical first IE of 8.05 eV (6e) obtained for the cubane-based geometry of **1a**, which increases to 9.25 eV (6e), close to the experimental value, for the optimized geometry.

6-Bromo- and 6-Iodotricyclo[3.1.1.0^{3,6}]heptane (1b and 1c). The experimental IEs of **1b** and **1c**, obtained from the time-averaged He I spectra shown in Figure 1, are listed in Table II, where they are compared with those of **1a**. Table II also includes the theoretical Koopmans IEs based on the VEOMP calculations for the three molecules.

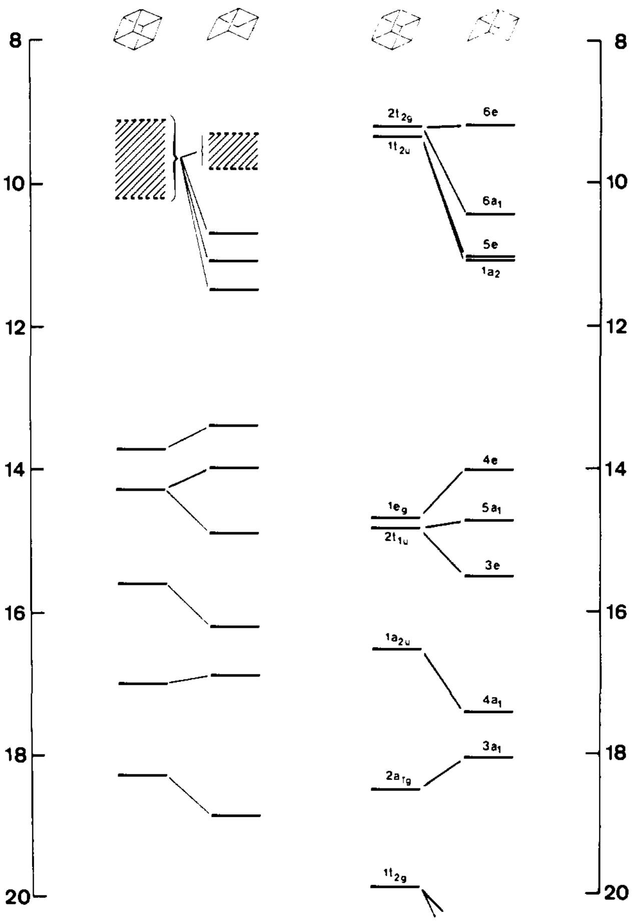


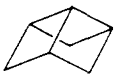
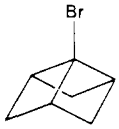
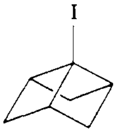
Figure 2. Comparison of the experimental and calculated correlation of the ionization energies of cubane and tricyclo[3.1.1.0^{3,6}]heptane.

The spectra of **1b** and **1c** are most atypical. Their observed spectral characteristics deviate considerably from those of the bicycloalkanes[8] owing to the different relative IEs of the alkane and halogen moieties and because the uppermost MO of **1a** is of e symmetry. The first PE band of 6-bromotricyclo[3.1.1.0^{3,6}]-heptane (**1b**) is clearly associated with the Jahn–Teller split first band of the unsubstituted alkane. Its band shape indicates that bromine contribution to the corresponding MO is minimal. However, the VEOMP calculations reported in the spectral assignment of Table II attribute considerable bromine composition to this MO (7e), but also significant bromine character in the deeper 6e and 5e MOs. The VEOMP calculation clearly indicates a spread of bromine character among the outer orbitals, but places most of this in 7e and 6e, while the assignment given in Table II suggests that 6e and 5e incorporate most of the bromine character.

An indication of the sensitivity of the VEOMP calculation to the quality of the atomic valence functions is shown in this example by changing the orbital exponent of the diffuse 4s and 4p functions for bromine from 0.5 to 1.0. The effect of this change is to stabilize the bromine 4p orbitals and redistribute their contributions in the MOs of e symmetry. The resulting bromine contributions to the 6e and 5e MOs of **1b** are 54 and 22%, respectively. Analysis of the MO coefficients indicates that these orbitals can be described as respectively antibonding and bonding combinations of localized n_{Br} orbitals with the proximate alkane orbitals. Hence the labels n_{Br}* and n_{Br} are used in Table II.

An interesting feature of the assignment is that the σ_{CBr} bond is assigned as the sharp band at 10.4 eV, of lower IE than the n_{Br}-based bands. This unusual result is suggested by the calcu-

Table II. Comparison of Experimental and Calculated Vertical Ionization Energies (in eV) and Molecular Orbital Assignments (C_{3v}) of Tricyclo[3.1.1.0^{3,6}]heptane (1a), 6-Bromotricyclo[3.1.1.0^{3,6}]heptane (1b) and 6-Iodotricyclo[3.1.1.0^{3,6}]heptane (1c)

								
exptl IE[a]	assignment MO[b]	VEOMP $-\epsilon$	exptl IE[a]	assignment MO[b]	VEOMP $-\epsilon$	exptl IE[a]	assignment MO[b]	VEOMP $-\epsilon$
9.3	6e	8.97	9.27	7e	9.18	8.79	(n_I) 7e	8.40
9.8			9.61		9.36	9.22		8.85
10.7	6a$_1$	10.30	10.4	(σ_{CBr}) 7a$_1$	10.60	9.97	(σ_{CI}) 7a$_1$	10.04
11.1	5e	10.76	10.6	(n_{Br}*) 6e	10.64	10.43	6e	10.49
11.5	1a$_2$	10.67	10.8		10.77	10.8		10.55
13.4	4e	13.77	11.8	1a$_2$	11.72	11.4	1a$_2$	11.84
13.9	5a$_1$	14.54	12.0	(n_{Br}) 5e	12.07	11.8	5e	12.05
14.9	3e	15.13	13.7	6a$_1$	14.46	13.6	6a$_1$	14.42
16.2	4a$_1$	17.46	14.2	4e	14.74	14.0	4e	14.85
16.9	3a$_1$	17.74	15.2	3e	16.25	15.1	3e	16.34
18.5	2e	20.48	15.8	5a$_1$	16.56	15.5	5a$_1$	16.58
			16.9	4a$_1$	18.49	16.8	4a$_1$	18.60
			18.9	3a$_1$	21.25	18.9	3a$_1$	20.21

[a] Accuracies vary between ±0.01 and ±0.1 eV. [b] Orbital numbering within valence shell for C_{3v} point group.

lations as due to the proximity of the 6a$_1$ MO of **1a**. The fact that the 5a$_1$ MO of **1a** is rather distant at 13.9 eV indicates that 6a$_1$ is the logical MO to incorporate the bromine character. The admixture is probably of increased antibonding nature and results in an approximately nonbonding orbital reduced in IE by 0.3 eV in going from **1a** to **1b** and represented by the sharp band in the spectrum. Additionally, this band is similar to the analogous 7a$_1$ band of **1c** at 9.97 eV which is assigned as of mainly σ_{CI} character.

Since the cycloalkane C_{3v} symmetry is not lost upon halogen substitution, the operation of SO coupling would be expected. This is not clearly observed in the PE spectrum being offset by the sharing of bromine character between the two MOs of e symmetry. This is verified in the VEOMP calculations where the calculated splittings in the orbitals of e symmetry are 0.18 and 0.13 eV. These results suggest that the small peaks at 10.6 and 10.8 eV can be assigned to the SO-split 6e orbitals.

The PE spectrum of 6-iodotricyclo[3.1.1.0^{3,6}]heptane (**1c**) is unique among the iodocycloalkanes in placing the SO split component of the first band, corresponding to the maximum iodine valence 5p interaction with the alkane moiety, at lower IE. This feature is attributed to the increased conjugation between alkane and halogen MOs brought about both by the proximity of their energies, and the suitability of the uppermost e MO of **1a** for interaction. The broadened peak at 8.79 eV is then associated with maximum conjugation, and iodine character is lent to the peak at 9.97 eV. The splitting of 0.43 eV observed for this doublet is among the smallest measured for iodoalkanes, consistent with a reduction in the influence of SO coupling. The VEOMP calculation simulates this effect and shows the influence of conjugative interactions via the second-order contributions to the SO splitting. So a first-order separation of 0.49 eV is reduced to 0.45 eV with second-order contributions, close to the experimental value. Iodine contribution to the 7e MO is calculated to be 73%, significantly lower than for the n_I MOs of other iodocycloalkanes. The calculated iodine contribution to the 6e MO is 10%, but in view of the observed band structure this result is likely to be an underestimate. Inclusion of SO coupling in the calculation yields a cationic state with 32% iodine composition.

The location of the σ_{CI} MO at 9.97 eV (7a$_1$) represents a destabilization by 0.7 eV of the 6a$_1$ MO of **1a** at 10.7 eV, and is roughly matched by the VEOMP calculated destabilization of 0.26 eV. In the acyclic alkyl iodides the σ_{CI} MO is essentially bonding, being stabilized by resonance interaction of I5p with a high IE alkane orbital. By contrast, in **1c** the low IE alkane orbital available leads to destabilization of I5p and an approximately nonbonding MO is the result.

Bromo- and Iodocubane (2b and 2c). Interest in the electronic structure of cubane (**2a**) due to its high symmetry and considerable strain has prompted a comprehensive analysis of both He I and He II PE spectra by Bischof et al.[10] Extensive overlap of the bands assigned to the ionization of electrons from the highest occupied t_{2g} and t_{2u} MOs of cubane is complicated by Jahn–Teller distortions of the cation. The t_{2u} MO is calculated to be localized entirely on the cubic carbon framework.

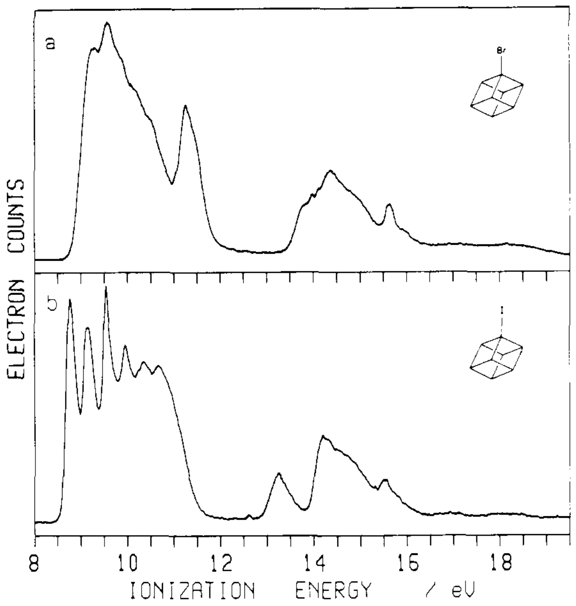
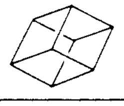
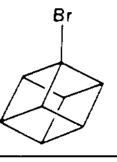
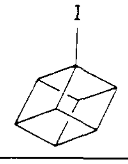


Figure 3. The He I photoelectron spectra of (a) bromocubane and (b) iodocubane, at sample temperatures of 40 °C.

Halogen substitution lowers the molecular symmetry to C_{3v} and thus introduces the possibility of interaction between the t_{2u} and t_{2g} MOs. VEOMP calculations on iodocubane (**2c**) suggest that the iodine p orbitals retain their nonbonding character with the n_I MOs being 88% iodine in composition. The bromine p orbitals of bromocubane (**2b**) interact more strongly with components of the t_{2u} MOs which have carbon p orbitals at the substituent site directed perpendicular to the C–Br bond. Bromine contribution to the n_{Br} MOs is thus reduced to 70%. This distinction is evident in the band shapes observed at low IE in the PE spectra of **2b** and **2c** shown in Figure 3. While the 9- to 11-eV region of the spectrum of **2b** has little distinctive structure, the corresponding section of the **2c** spectrum is dominated by several prominent peaks to which nonbonding character can be attributed. The VEOMP results suggest that SO interactions which lift the degeneracy of the ground ionic state are responsible for the first two peaks which

Table III. Comparison of Experimental and Calculated Vertical Ionization Energies (in eV) and Molecular Orbital Assignments of Cubane (O_h) (2a), Bromocubane (C_{3v}) (2b), and Iodocubane (C_{3v}) (2c)

				 			 	
exptl IE[a]	assignment MO[b]	VEOMP $-\epsilon$	exptl IE[c]	assignment MO[d]	VEOMP $-\epsilon$	exptl IE[c]	assignment MO[d]	VEOMP $-\epsilon$
9.0 9.6	$2t_{2g}$	9.00	9.3	(n_{Br}*) 7e	9.12 9.28	8.76 9.15	(n_I) 7e	8.33 8.76
			9.6	(σ_{CBr}) $8a_1$	9.93	9.52	(σ_{CI}) $8a_1$	9.54
9.9	$1t_{2u}$	9.13	10.1	$1a_2$	10.10	9.97	$1a_2$	10.24
			10.5	6e	10.13	10.38	6e	10.25
13.7	$1e_g$	14.25	11.3	(n_{Br}) 5e	10.95 11.07	10.70	5e	10.73
14.3	$2t_{1u}$	14.53	13.8	$7a_1$	13.51	13.3	$7a_1$	13.30
15.6	$1a_{2u}$	16.68	14.4	4e	15.43	14.2	4e	15.55
17.6	$2a_{1g}$	18.15	14.9	3e	15.61	14.7	3e	15.73
18.5	$1t_{2g}$	19.81	15.6	$6a_1$	17.02	15.5	$6a_1$	17.11
			17.1	$5a_1$	18.46	16.9	$5a_1$	18.45
			18.3	$4a_1$	19.87	18.1	$4a_1$	19.73

[a] From the spectrum in ref 10. [b] Orbital numbering within valence shell of O_h point group. [c] Accuracies vary between ±0.01 and ±0.1 eV. [d] Orbital numbering within valence shell for C_{3v} point group.

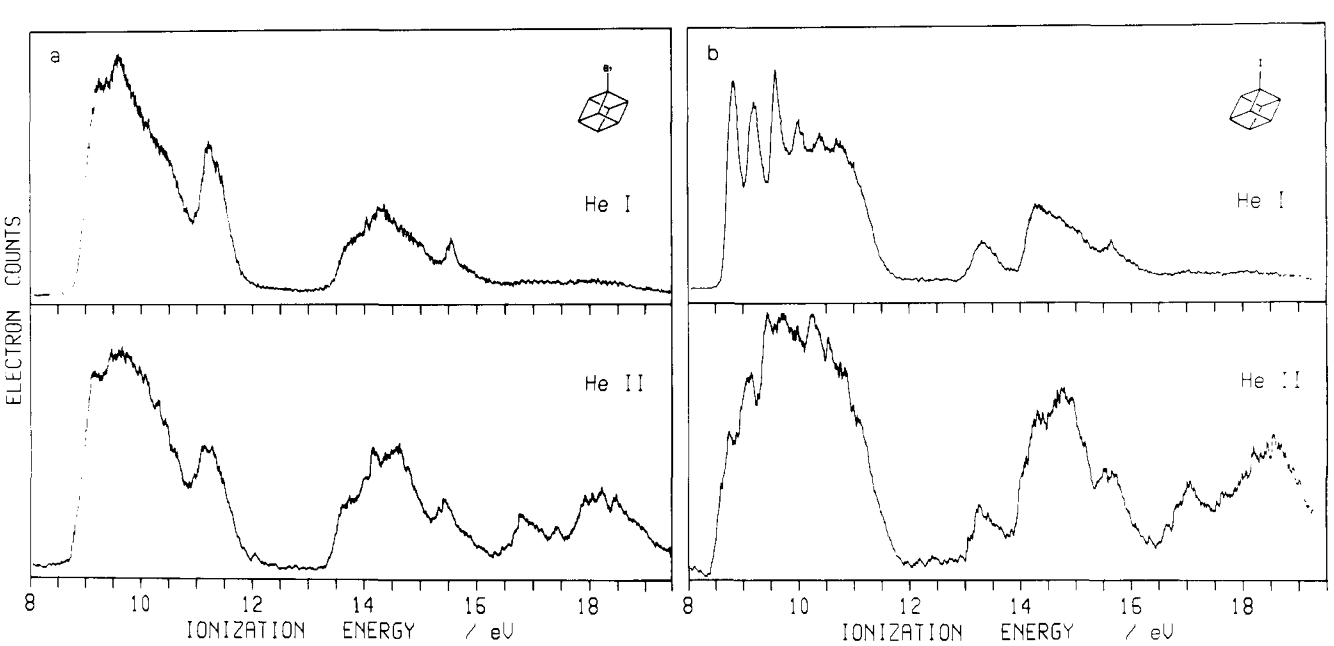


Figure 4. Single-sweep He I and He II photoelectron spectra of (a) bromocubane and (b) iodocubane.

are separated by 0.39 eV. Reduction from the splitting observed in typical n_I bands is due to increased interaction between the $E_{1/2}$ component of the SO split cationic state, which lies at higher IE than the $E_{3/2}$ component, and the A_1 state, which is transformed to $E_{1/2}$ in the double point group. The calculation gives a first-order splitting of 0.53 eV which reduces to 0.43 eV on inclusion of second-order effects. The $e_{1/2}$ component of the 7e MO is calculated to contain 13% of the $8a_1$ MO and this is responsible for the 0.10-eV shift. Table III provides a comparison of experimental and calculated IEs of **2b** and **2c** and allows a correlation of their IEs with those of **2a**.

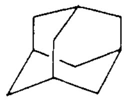
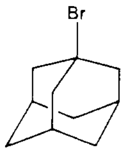
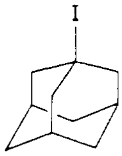
Diminished bromine contribution to the 7e MO of **2b** due to interaction with components of the **2a** t_{2u} MOs is reflected in a concomitant increase in bromine character in the 5e MOs. The VEOMP calculation attributes 39% bromine character to these 5e MOs, and the PE spectrum, with an intense band at 11.3 eV, is consistent with this result. Analogous to the description for **1b**, these antibonding and bonding combinations of bromine and alkane orbitals are characterized by the notations n_{Br}*(7e) and n_{Br}(5e).

A σ_{CI} MO results from a combination of the iodine 5p orbital aligned along the C–I bond and a t_{2g} component of **2a**. Being of a_1 symmetry it is not a candidate for SO splitting, but, as indicated above, its cationic state may interact with the SO split E state. This cationic state is assigned to the PE band at 9.52 eV. In the PE spectrum of **2b** the ionization of a σ_{CBr} bonding orbital is assigned to 9.6 eV where considerable band overlap obscures its precise location.

Reduction in relative intensity is the principal feature of the low IE regions of the He II spectra of **2b** and **2c** as seen in Figure 4. Comparison of the He I and He II spectra support the assignment of ionization of MOs with significant bromine character to bands located near 9 and 11 eV since their intensity decreases relative to the 9.5- to 10.5-eV region in the He I spectrum. The **2c** He II spectrum displays the expected diminution between 9 and 10 eV.

There exists a close relationship between the high IE regions of the PE spectra of **2b** and **2c** and that of **2a**.[10] The inductive effect of halogen substitution is seen in a stabilization of **2a** MOs by an average of 0.4 eV in **2b** and 0.2 eV in **2c**. An exception

Table IV. Comparison of Experimental and Calculated Vertical Ionization Energies (in eV) and Molecular Orbital Assignments of Adamantane (T_d) (3a), 1-Bromoadamantane (C_{3v}) (3b), and 1-Iodoadamantane (C_{3v}) (3c)

								
exptl IE[a]	assignment MO[b]	VEOMP $-\epsilon$	exptl IE[c]	assignment MO[d]	VEOMP $-\epsilon$	exptl IE[c]	assignment MO[d]	VEOMP $-\epsilon$
9.55	$5t_2$	9.44	9.63 9.85	(n_{Br}) 10e	9.28 9.50	8.79 9.26	(n_I) 10e	8.28 8.76
10.95	$2t_1$	11.07				9.81	(σ_{CI}) $8a_1$	9.59
11.3	2e	11.07	10.2	(σ_{CBr}) $8a_1$	10.02	10.2	9e	10.46
			10.5	9e	10.40			
13.0	$4t_2$	13.41	11.4	$3a_2$	11.86	11.2	$3a_2$	11.99
13.4	$1t_1$	13.87	11.6	8e	11.93	11.4	8e	12.05
14.85	$3t_2$	15.52	11.8	7e	12.29	11.6	7e	12.34
15.5	$3a_1$	16.43	13.2	(σ_{CBr}) $7a_1$	12.76	12.7	(σ_{CI}) $7a_1$	12.61
16.96	$2a_1$	17.97	13.5	6e	14.25	13.4	6e	14.39
18.5	$2t_2$	20.40	13.7	$2a_2$	14.73	13.7	$2a_2$	14.87
			14.0	5e	14.84	13.9	5e	14.95
			15.2	$6a_1$	16.05	15.1	$6a_1$	16.14
			15.4	4e	16.42	15.3	4e	16.56
			15.6	$5a_1$	16.49	15.5	$5a_1$	16.60
			17.3	$4a_1$	18.69	17.2	$4a_1$	18.70
			18.5	$3a_1$	19.78	18.1	$3a_1$	19.38

[a] From the spectrum in ref 11. [b] Orbital numbering within valence shell for T_d point group. [c] Accuracies vary between ±0.01 and ±0.1 eV. [d] Orbital numbering within valence shell for C_{3v} point group.

is the $7a_1$ MO, which incorporates some σ_{CX} character arising from conjugative interaction between the t_{1u} MO of **2a** and the halogen p orbital directed along the C–X bond. The detachment of the associated PE band from the cubane spectral structure increases from bromo to iodo substitution, in keeping with the relative electronegativities of bromine and iodine.

1-Bromo- and 1-Iodoadamantane (3b and 3c). Interest in the electronic structure of adamantane (**3a**) has been promoted by its almost strain-free molecular structure. As a result **3a** and several of its derivatives have been subjected to investigation by PE spectroscopy.[9,13] Both He I and He II spectra of **3a** have been reported.[11,12] The high symmetry of the molecule should simplify its PE spectrum, but concomitant with high symmetry is a susceptibility to Jahn–Teller distortions which may complicate the one-to-one assignment of cationic states to PE bands. Kovac and Klasinc[13] have demonstrated that Jahn–Teller active vibrational modes are excited in several of the ionic states of **3a**, producing Jahn–Teller splittings which attain a maximum value of 0.5 eV in the first PE band.

Halogen substitution at a bridgehead position of **3a** lowers its symmetry to C_{3v}, but the degenerate ionic states produced by ionization of the molecule may still be subject to the Jahn–Teller effect. The assignment of the PE spectra of 1-bromoadamantane (**3b**) and 1-iodoadamantane (**3c**), shown in Figure 5, are given in Table IV. These result from VEOMP MO calculations and correlations with the IEs of **3a** which are also listed. The band groupings predicted by the VEOMP calculations agree well with the PE band contours, with the exception of their location of the second σ_{CX}-type band near 13 eV. It is clear from a comparison of the **3b** and **3c** spectra that a band on the low IE side of the 13- to 14-eV region of the **3b** PE spectrum shifts into the otherwise band-free region at 12.7 eV with iodine substitution. While grouping these MOs with the band structure in the 11- to 12-eV region the VEOMP calculation does, however, reproduce the correct trend in their IEs.

Assignment of the bromine character to the 9.6- to 10.2-eV region of the **3b** spectrum is verified by its considerable increase in intensity relative to the same region of the **3a** spectrum. This band grouping suffers a diminution of relative intensity with He II ionizing radiation, most noticeably on its low IE perimeter. The location of the n_{Br} and σ_{CBr} bands is thus confirmed. The VEOMP calculation predicts splitting of 0.22 eV (reduced from a first-order value of 0.26 eV) in the n_{Br} orbitals (10e), in agreement with the experimental value of 0.22 eV.

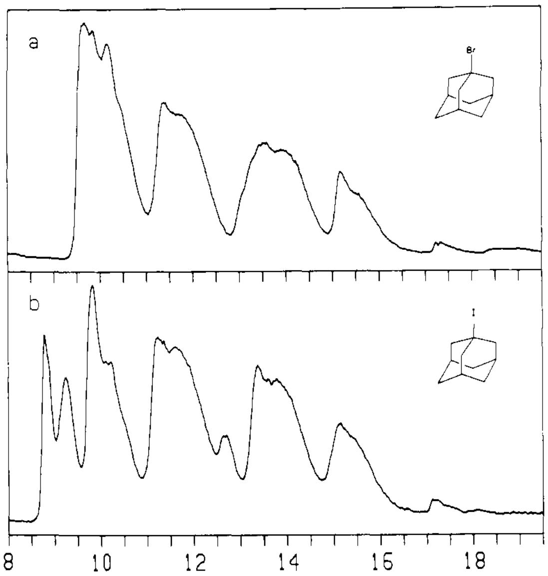


Figure 5. The He I photoelectron spectra of (a) 1-bromoadamantane at a sample temperature of 80 °C, and (b) 1-iodoadamantane at a sample temperature of 65 °C.

The first σ_{CBr} band at 10.2 eV originates in an antibonding combination of the bromine 4p orbital directed along the C–Br bond and the appropriate component of the uppermost $5t_2$ orbitals of **3a**. Relative intensity reduction with He II radiation also supports the assignment of the second σ_{CBr} band at 13.3 eV. This involves a bonding combination of bromine 4p and a component of the $4t_2$ orbitals of **3a**.

While the n_{Br} bands are embedded in the low IE spectral structure of the **3b** spectrum, the n_I orbitals again stand alone at low IE in **3c**. Spin–orbit interactions are mainly responsible for lifting the degeneracy of the ionic state though Jahn–Teller distortion may be an additional cause of the broadening of the component at higher IE. The VEOMP calculation accurately determines the SO splitting in the 10e band as 0.48 eV (reduced from a first-order value of 0.60 eV) in comparison with the observed separation of 0.47 eV. The second-order SO coupling involves an admixture of 13% of the $8a_1$ ($e_{1/2}$) orbital with the $e_{1/2}$ component of 10e. This result suggests that Jahn–Teller distortions are not required to explain the observed patterns. The σ_{CI} band is prominent at 9.81 eV and, together with the n_I bands and the second σ_{CI} band at 12.7 eV, is reduced in relative intensity under photoionization by He II radiation.

Inductive electron withdrawal by the bromine and iodine atoms is again responsible for stabilization of the MOs of **3a**. Exceptions arise when the halogen orbitals are of appropriate symmetry and energy for conjugative interaction with the alkane MOs. The resulting destabilization brought about by the resonance electron donation of the halogen atoms offsets their inductive effect, and in the case of the σ_{CI} MOs causes an overall destabilization.

Conclusion

The bromo and iodo derivatives of the polycycloalkyl halides considered in this study are each substituted at a tertiary carbon atom and are of C_{3v} symmetry. Consequently their He I photoelectron spectra show similarities to those of *tert*-butyl bromide and *tert*-butyl iodide. However, the competition between conjugative and spin–orbit coupling effects which influence the ionization energies and the splittings observed for the halogen bands in each spectrum show interesting variations which are difficult to simulate by molecular orbital calculations. An indication of the complexities involved is that while the bromine 4p orbitals lose their localized nonbonding character except for one sharp peak in **1b**, the iodine 5p orbitals exhibit considerable localized character, though in varying amounts. The 6-bromotricyclo-[3.1.1.0^{3,6}]heptane molecule (**1b**) is unusual in that its first photoelectron band is essentially of hydrocarbon character. In each of **1c**, **2c**, and **3c**, the σ_{CI} band is distinctive in that it is relatively narrow and intense in the He I spectra. The VEOMP calculations accurately simulate the observed splittings in the first PE band of the iodo compounds and indicate that the inclusion of second-order effects is necessary to explain the reduced separations obtained experimentally. In the halo adamantanes **3b** and **3c** the σ_{CX} bonding character is shared between two orbitals of a_1 symmetry. This is supported both by variations in their He I spectra and comparisons made with their He II spectra. The quality of calculations required to explain these observations in more detail is beyond present capabilities for molecules of the size represented here. Electrooxidation studies on these iodopolycycloalkanes[24] give $E_{1/2}$ values which correlate poorly with the first IEs measured here. The $E_{1/2}$ (IE) values for iodoadamantane (**3c**) are 1.72 V (8.79 eV) which show the same correlation noted for the iodobicycloalkanes,[8] that IE − $E_{1/2}$ = 7.09 ± 0.02. By comparison, **1c** with values of 1.52 V (7.27 eV) and **2c** with 1.57 V (8.76 eV) do not fit this pattern.

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Registry No. 1a, 51273-50-8; **1b**, 78995-60-5; **1c**, 74725-76-1; **2b**, 59346-69-9; **2c**, 74725-77-2; **3b**, 768-90-1; **3c**, 768-93-4.

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(24) R. S. Abeywickrema, E. W. Della, and S. Fletcher, *Electrochim. Acta*, **27**, 343 (1982).

Photoionization and Photohomolysis of Melanins: An Electron Spin Resonance–Spin Trapping Study

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Abstract: Electron spin resonance studies of the photolysis of synthetic and natural melanins in the presence of the spin trap 5,5-dimethyl-1-pyrroline 1-oxide are reported. Synthetic melanin was from autoxidation of dopa and natural eumelanin was extracted from bovine eyes. Spin adducts from reaction of transient species with the trap were identified and shown to arise from reaction with hydrated electrons and hydrogen atoms. It is inferred from this that e_{aq}^- and H· are products of melanin photolysis. Action spectra and quantum yields for these processes are reported and compared with those obtained for a synthetic melanin derived from catechol, which contains hydroxy aromatic, but no hydroxyindole, units.

Melanins are pigments derived from the enzymic oxidation of 3,4-dihydroxyphenylalanine (dopa) and/or cysteinyldopa.[1] They fall into two main classes: eumelanins, which are derived predominantly from dopa, and pheomelanins, which contain substantial amounts of units derived from cysteinyldopa. Natural melanins also contain protein. Following initial oxidation of the precursor, cyclization occurs, followed by polymerization to give a heterogeneous amorphous pigment. In eumelanins, the major units in the polymer appear to be based on 5,6-dihydroxyindole.[2]

Melanins function to protect tissue against the harmful effects of UV radiation.[3] However, damage to the pigment can occur during this process: photolysis of isolated pigments in air leads to the consumption of oxygen, which is reduced to superoxide and hydrogen peroxide, and associated pigment oxidation.[4] Recent quantitative data[5] have shown that the active chromophore is similar in both eumelanin and pheomelanin systems and that yields of net photooxidation are comparable. Thus photoinduced oxygen consumption is common to both classes of melanin.

The chromophore most active in oxygen consumption appears not to be the major eumelanin visible chromophore since the action spectrum for oxygen consumption[5,6] shows a much greater wavelength dependence than does the melanin optical absorbance

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(1) Prota, G. *J. Invest. Dermatl.* **1980**, *75*, 122–127.

(2) Nicolaus, R. A. "Melanins"; Hermann: Paris, 1968.

(3) Pathak, M.; Fitzpatrick, T. B. In "Sunlight and Man"; Fitzpatrick, T. B., Pathak, M. A., Harber, L. C., Seiji, M., Kukita, A., Eds.; University of Tokyo Press: Tokyo, 1974; p 725.

(4) Felix, C. C.; Hyde, J. S.; Sarna, T.; Sealy, R. C. *Biochem. Biophys. Res. Commun. 84*, **1978**, 335–341.

(5) Sarna, T.; Menon, I. A.; Sealy, R. C. *Photochem. Photobiol.*, in press.

(6) Sarna, T.; Sealy, R. C. *Photochem. Photobiol.* **1984**, *39*, 69–74.

0002-7863/84/1506-7327$01.50/0